

- ² J. R. Oppenheimer, *Z. Phys.*, **41**, 268 (1927).
³ P. S. Epstein, *Ann. Phys.*, **50**, 815 (1916).
⁴ P. S. Epstein, *Proceedings Amsterdam*, **23**, 1194 (1921).
⁵ E. Schroedinger, *Ann. Phys.*, **79**, 367 (1926).
⁶ P. S. Epstein, *Proc. Nat. Acad. Sci.*, **12**, 629 (1926). We shall refer to this paper as loc. cit.
⁷ μ, e mass and charge of electron, Z atomic number, $K = h/2\pi$.
⁸ This integral is a linear combination of Schroedinger's two integrals, V_1 and V_2 .
⁹ G. Temple, *Proc. Roy. Soc.*, **121**, 673 (1928).
¹⁰ P. S. Epstein, *Phys. Rev.*, **28**, 69 (1921). I seize this opportunity for stating that, owing to an oversight, a factor 2 is missing in that paper in the intensity expressions of all those components for which I am indebted to Mr. Slack for drawing my attention to this omission.
¹¹ This formula is due to Sonin (*Math. Ann.*, **16**, 40, 1880). See, also, N. Nielsen, *Cylinderfunktionen*, p. 184. Leipzig, 1934.
¹² C. F. Gauss, *Werke*, Vol. III, p. 213. Goettingen, 1876.
¹³ In this formula the first letter e represents the basis of natural logarithms, the second the charge of the electron.

ON A FLUORESCENCE SPECTRUM OF OXYGEN

BY F. RASETTI

NORMAN BRIDGE LABORATORY OF PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated April 2, 1929

The spectrum of the light from a mercury arc scattered by oxygen at atmospheric pressure and photographed with a quartz spectrograph shows, besides the Raman lines which have been reported by the writer in other notes,¹ a series of doublets, extending from the ultra-violet limit of the spectrum on the plate down to the visible region. This appears as a fluorescence spectrum excited by the resonance line $\lambda 1849$ of mercury, which is strongly absorbed in O_2 .

As it seems that this fluorescence of oxygen had never been noticed before, probably because of its extreme weakness, exposures of 50 to 80 hours being needed to bring it out, and, as on the other hand, I have been able to determine its relationship with the known O_2 bands, I will give a brief account of the results obtained.

A large Hilger quartz spectrograph was used. Wave-lengths were measured by comparison with an iron arc spectrum to an accuracy ranging from $\pm 0.3 \text{ \AA}$ in the visible to ± 0.1 in the far ultra-violet.

Before giving the observed wave-lengths of the lines, it is better to explain the general structure of this spectrum.

From Ossenbrüggen's work,² we know very well the structure of the Schumann-Runge band system of O_2 , a $^3S \rightarrow ^3S$ transition, according to

Mulliken.³ The lower electronic state has only odd and the upper only even rotational states, so that each band consists only of a *P*- and *R*-form branch.

Now, from Ossenbrüggen's data, we see that the frequency of the $\lambda 1849$ mercury line, 54065.7 cm.^{-1} , coincides practically with two absorption lines of the Schumann-Runge system, precisely in Ossenbrüggen's notations with the lines:

$$R_{80}(11) = \nu_0(8,0) + F_8(12) - f_0(11) = 54064 \text{ cm.}^{-1}$$

$$P_{80}(9) = \nu_0(8,0) + F_8(8) - f_0(9) = 54068 \text{ cm.}^{-1}$$

where $\nu_0(8,0)$ represents the energy of the transition between the zero vibrational state of the lower electronic level and the eighth vibrational state of the upper electronic level; and F and f are the rotational energies of the two states.

So we have to expect to observe in emission all the allowed combinations of the 8th vibrational and 8th and 12th rotational states with lower levels.

All the intense observed lines can be explained as combinations with the second of these levels. According to the selection rule $\Delta j_k = \pm 1$, we should observe the following combinations in emission:

$$R_{8k}(11) = \nu_0(8,k) + F_8(12) - f_k(11) \quad (1)$$

$$P_{8k}(13) = \nu_0(8,k) + F_8(12) - f_k(13) \quad (2)$$

where $k = 0, 1, 2, 3, \dots$ represents the vibrational state of the lowest electronic level.

Part of the frequencies of the "zero lines" $\nu_0(8,k)$ are known from direct observation, and the others can be calculated very accurately from the formula for the energy of the k vibrational state:

$$(E_k - E_0)/hc = 1565.37.k - 11.37.k^2$$

while the terms $F(j_k)$, of the form $Aj_k(j_k + 1)$, are all given by Ossenbrüggen.

The observed values of k range from 8 to 22, but there is an irregular variation of the intensity, and some lines could not be observed at all. This appears from the following table:

		TABLE I	
k	CHARACTERISTICS OF THE DOUBLET	k	CHARACTERISTICS OF THE DOUBLET
8	intense	16	missing
9	intense	17	missing
10	weak	18	intense
11	extremely weak	19	intense
12	intense	20	? (overlapping with strong Hg lines)
13	weak	21	intense
14	missing	22	intense
15	weak		

Table II gives the observed values of the frequencies in cm^{-1} , the calculated values according to formulas (1) and (2), and the difference between them.

	CALC.	$R_{8k}(11)$ OBS.	DIFF.	CALC.	$P_{8k}(13)$ OBS.	DIFF.
8	42285.2	42279.5	- 5.7	42219.7	42217.2	- 2.5
9	40915.1	40915.0	- 0.1	40850.4	40851.3	+ 0.9
10	39567.8	39503.8	39503.8	0
12	36942.0	36939.0	- 3.0	36879.6	36874.5	- 5.1
13	35662.9	35601.4	35596.1	- 5.3
15	33172.9	33167.6	- 5.3	33112.8	33110.3	- 2.5
18	29608.9	29605.8	- 3.1	29551.4	29548.2	- 3.2
19	28466.2	28465.1	- 1.1	28409.3	28409.9	+ 0.6
21	24249.1	26257.1	+ 8.0	24193.9	26204.1	+10.2
22	25174.7	25194.7	+20.0	25120.2	25139.5	+19.3

From the table, it appears that the calculated and observed values agree within the limits of experimental error, except for the last two doublets. But we may expect the simple quadratic formula for the energies E_k to become inaccurate for high values of the vibrational quantum number. The discrepancy is not *much* larger than the experimental error in this region, anyhow. The frequencies of two lines are not given as they practically overlap with mercury lines.

The characteristic doublet structure with a separation of about 60 cm^{-1} of this fluorescence spectrum is very accurately accounted for as a $f_k(13) - f_k(11)$ doubling.

We should expect, also, doublets having the 8th rotational state as initial level to occur. One component of these doublets, that is, $P_{8k}(9)$, falls always so close to $R_{8k}(11)$ that it cannot be separated with the resolution available. The other, $R_{8k}(F)$, should fall at about 40 cm^{-1} distance on the short wave-length side of $R_{8k}(11)$. Near the stronger of the doublets, a line was actually observable in that region, but it is too weak to be measured accurately.

We may remark that this fluorescence spectrum seems to have somewhat different characteristics from the well-known atomic fluorescent spectra, and the J_2 fluorescence in the case of molecules. We should expect the fluorescence to occur with higher intensity at low pressure, but an experiment with oxygen at about 8 mm. pressure gave no lines at all. On the other hand, at atmospheric pressure the time between impacts is short compared with the mean lifetime of the molecule in excited states, so that impacts of the second kind should distribute the molecules in a number of rotational states, and the emission should consist of the whole bands instead of only two lines of each. So we have perhaps an instance of a transition case between Raman effect and fluorescence, or what we might call a "selective Raman effect."

As the frequency ν of the impinging quantum becomes very near to the characteristic absorption frequency $(E_k - E_i)/h$, the scattering (both of unmodified and modified frequency) becomes particularly intense, and in the Raman spectrum those transitions $i \rightarrow s$ are particularly enhanced, for which the transition probability (ks) is high. So we might consider the observed frequencies, also, as differences between the frequency of the Hg line λ 1849 and the frequencies of the considered transitions. The values calculated in this way would differ only by 1.7 cm.^{-1} from those given above, which falls within the limits of accuracy of the present measurements. In this way, we might account for the fact that only two lines of each band appear at such high pressure. The above-given classification of the observed lines holds both if we consider the phenomenon as a fluorescence or as a Raman effect.

I am glad to acknowledge my indebtedness to the International Education Board for a fellowship grant which gave me the possibility of working at the California Institute of Technology.

¹ F. Rasetti, *Proc. Nat. Acad. Sci.*, **15**, 234, 1929; *Nature*, April, 1929.

² W. Ossenbrüggen, *Zeit. Phys.*, **49**, 167, 1928.

³ R. S. Mulliken, *Phys. Rev.*, **32**, 186 and 880, 1928.

ON THE SPECTRA OF ZNII, CDII, INIII AND SNIV

BY R. J. LANG

DEPARTMENT OF PHYSICS, UNIVERSITY OF ALBERTA

Communicated March 24, 1929

Abstract.—In the spectrum of ZnII six new combinations between known terms are located. In CdII the 7S term is found, and two inter-combinations are recorded. In InIII one new multiplet, based on known term values, is given and possible values for the 6F terms obtained. In SnIV four multiplets are located all based upon previously known term values.

The spectra of ZnII and CdII were investigated by G. v. Salis¹ in 1925, who found a large number of terms based upon the normal configuration (d^{10} ZnIII, CdIII) and one anomalous doublet D term from (d^9s^2) of ZnII but only one of this pair of terms in CdII. At that time the Hund theory was not developed and the meaning of these anomalous terms was not known; nor had the Schumann region been accurately measured, so that the classification of Salis did not extend far beyond 2000 Å.

InIII and SnIV have been classified by Carroll,² Rao³ and the writer⁴ while Rao, Narayan and Rao⁵ have recently summed up the known terms